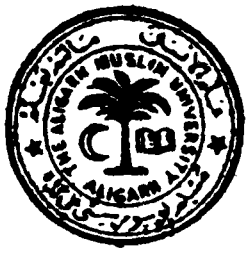

STUDIES ON INORGANIC ION EXCHANGERS AND LIGAND ION EXCHENGERS

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

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IN

CHEMISTRY

BY

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1994

Dedicated
To My
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CERTIFICATE

This is to certify that the work embodied in this dissertation entitled, **"Studies on Inorganic Ion Exchangers and Ligand Ion Exchangers"** is original work carried out by **Miss Uzma Naseer** under my supervision and is suitable for submission for the award of M.Phil degree in Chemistry of this University.

J P Rawat

(J.P. RAWAT)

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Uzma Naseer

January 1995 **UZMA NASEER**

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CHAPTER - I

I N T R O D U C T I O N

INTRODUCTION

Analytical chemistry deals with the development of methods for identification, separation and determination of the substances. Identification of substances constitutes the branch qualitative analysis and determination forms the branch quantitative analysis. Generally, the separation is the pretreatment procedure for most of the determinations and sometimes for identifications. Thus all the three techniques together form the subject of chemical analysis. Chemical analysis is based upon classical and modern methods of analysis. The modern methods of analysis are divided into two broad groups viz - instrumental and non-instrumental. Instrumental techniques find their application in quite a number of interesting work being carried out today. The non-instrumental techniques too are equally important in tackling various problems and are less expensive. The non-instrumental techniques are developed mainly for achieving separations. The various methods that are employed for separation are chromatography, electrophoresis, ion-exchange solvent extraction, ring oven techniques and dialysis etc. Bery has given a concise account of such methods in his book entitled "Physical and Chemical Methods of Separation".1

Ion exchange is one of the most versatile techniques of separation science. It is at present, an standard analytical tool and is widely used in inorganic, organic and biochemical separations. It offers many advantages over the

classical methods of separation such as precipitation, distillation and filteration. This technique can be applied to both micro as well as macro analysis and may serve even for the routine analysis. It demands less skill and judgement from the analyst than many other methods. Furthermore, a shorter time is needed and the components can subsequently be determined by rapid instrumental or titrimetric methods. It is of great significance when one is concerned with the separation of ions of similar properties or the systems which are troublesome or impossible to analyze by other methods.

In laboratories ion exchangers are being used as an important tool to solve new problems that are placed by our industrialists and scientists. All over the world numerous ion exchanger plants are in operation for developing the separation of various mixtures of inorganic, organic and biological interest. Rapid and accurate determination of the constituents of a sample or contaminants of alloys of complicated compositions, biological substances and fission products of radioactive elements has become possible bythe use of ion exchangers. It has made possible the chromatographic separation of very complicated mixtures. This technique has been used to solve previously unsolvable problems such as separation of rare earths and recovery of rare elements. The use of ion exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of important metals and raw

materials which are becoming more and more difficult to produce. Ion exchange has established itself as one of the most powerful techniques in the field of water analysis, thus providing its worth in water pollution control.

Soil, an expensive, natural and easily available material was for the first time recognised as an ion exchange material. Nearly 150 years ago an English landowner H.S. Thompson was interested to study the loss of ammonia from manure heaps. He engaged a york scientist named Spence to investigate this loss. Spence discovered this loss as an exchange process between calcium (from soil) and ammonia (from manure).

$$Ca^{2+}\ (Soil) + (NH_4)_2SO_4 \rightleftharpoons NH_4^+\ (Soil) + CaSO_4 \quad ...(1)$$

Spence reported his discoveries to the Royal Agricultural Society[2]. These were further confirmed by another agricultural chemist G.T. Way[3] who described this exchange by the name of "base exchange". The base exchange in soils was found to be reversible and stoichiometric. This phenomena could not be elaborated further as much was not known about the ionic nature of solutions and the crystal structure and composition of the clay minerals present in the soil, many hypotheses were given to explain this exchange in soils[4], but ultimately it was traced mainly due to presence of aluminosilicates[5,6]. According to Lamberg[7] and Weigner[8] the materials responsible for the exchange in soils were mainly clays, zeolites, glauconites, humins and

humic acid. The glauconites are also aluminosilicates analogous to the zeolites which possess exchangeable potassium and considerable capacity. The first aluminosilicates were synthesized by Harms and Rumpler[9] in 1903. The two principal causes responsible for ion exchange property of soils are organic matter and clay minerals. The soils rich in organic matter contain humins and humic acid which on decomposition produce a wide variety of organic species possessing -OH or -COOH groups. These groups are responsible for the ion exchange property in such soils. The soils which do not contain much organic matter or whose organic matter has been destroyed by the treatment of hydrogenperoxide also possess a considerable ion exchange property due to the presence of crystallographic surfaces (clay minerals) with exchangeable sites.

A search for stable ion exchanger was started to overcome the limitations possessed by zeolites and clays. In 1931 Kullgren found that copper was taken up by sulfite cellulose when the cellulose was washed with distilled water[10]. He used this material for the removal of copper present in water as a contaminant. Organic ion exchangers were recognised after an interesting discovery of Adams and Holmes in 1935. They found that crushed phonograph records exhibit ion exchange properties. This led them to the synthesis of organic ion exchange resins[11] which exhibited an improved properties over the previously known ion exchangers. These resins consist of three dimensional networks of polymeric chains cross-linked with short chains

containing ionizable functional groups. Various improvements were made in these resins. A typical resin is prepared by polymerization of styrene and divinyl benzene. The number of cross-linkage is governed by divenylbenzene to styrene ratio. A representative type of strong cation exchange resin is Dowex 50W x 8, manufactured by Dow Chemical Co., Midland, Mich. Organic ion exchange resins are stable towards acids and elegant to handle. Their structure can be varied as desired. An increase in cross-linkage increases the rigidity, reduces swelling and reduces the solubility of polymeric structure. Organic resins have been used in laboratories and industries for separations, recoveries of metals, purification of water, concentration of electrolytes and elucidation of the mechanism of great many reactions. Several commercial resins, both cation (strong and weak acid) and anion (strong and weak base) exchangers are available for these purposes. A third type is amphoteric ion exchange resin with only a few applications.

Organic ion exchangers also suffer from certain limitations. They are unstable in aqueous system at high temperatures and in presence of ionizing radiations. This led to a revived interest in inorganic ion exchangers. Inorganic ion exchangers are unaffected by ionizing radiations and considerably temperature resistant. This makes them suitable for use in reactor technology. Their rigid structure makes them more suitable for separation of ions on the basis of different pore sizes. They can also be

used as ionic or molecular sieves. High selectivity and temperature resistance offer them an advantage for use as ion exchange membranes. Their selectivity has also been utilized for the preparation of ion selective electrodes which has now become an important tool for solving various analytical problems.

Systematic and fundamental studies on inorganic ion exchangers commenced in 1943 with the application of zirconium phosphate to the separation of uranium and plutonium from fission products[12]. Zirconium phosphate is perhaps the most studied inorganic ion exchanger. Other inorganic ion exchangers with satisfactory properties have been prepared by combining group IV oxides with more acidic oxides of group V and VI. Various inorganic ion exchangers reported upto 1964 have been excellantly reviewed in a monograph of Amphlett[13] entitled "inorganic ion exchangers" which has become a classic in this field. The different types of ion exchange materials are summarised in the following broad groups.

1. clay minerals
2. Zeolites
3. Heteropoly acid salts, and
4. Hydrous oxides and insoluble salts.

Literature data on a new series of synthetic inorganic ion exchangers has been compiled of Ionescu[14] considering in this study the salts of heteropoly acids, the oxides and hydroxides of polyvalent metals and some

particular compounds such as polyphosphates, ferrocyano molybdates and mixed ferrocyanides of light and heavy metals. Representative types of inorganic ion exchangers have been reviewed by Ito and Abe[15]. The theoretical ion exchangers have been described by Marinsky[16]. The work done in the period between 1963 and 1970 have been summerized by Pekarek and Vasely[17,18] under the following categories :

1. Hydrous oxides
2. Acidic salts of polyvalent metals
3. Salts of heteropolyacids
4. Insoluble ferrocyanides
5. Double salts

A review on zirconium phosphate ion exchangers polybasic salts other than zirconium phosphate and the salts of heteropolyacids and hydrous oxides has been given by Clearifield[19]. M. Abe[20] has summ rized the ion exchange characteristics of salts containing polyvalent elements of group III, IV, V and VI. Marinsky[21] and Walton[22] have edited the reviews on the application of inorganic ion exchangers. Synthesis and application of inorganic ion exchangers have been reviewed by Walton[23-27]. The recent trends in the field of ion exchange have been summarized in the "Journal of Chromatography" volume 102(1974), which contains the papers presented at the third symposium on ion exchange held at Balat ɔnfired (Hungary) May 28-31, 1974. The papers presented were divided into four sections.

1. Ion exchange materials

2. Theory of ion exchange
3. Analytical applications, and
4. Ion exchange technology.

The synthesis of new materials have been reported by numerous authors defining different materials. The zirconium phosphate is the most studied of all the ion exchangers. A review with the emphasis on zirconium phosphate has been recently presented by Gracia et al.[28] Recent work on inorganic ion exchange materials has been covered in a monograph of Clearfield[29]. Recently, a comprehensive review on different types of synthetic inorganic ion exchangers and their properties have been reported[30-31]. Synthesis and ion-exchanger properties of the such ion exchangers are as follows :

Table - A

Synthesis and Properties of two component ion exchanger

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
	i) Zirconium based ion exchangers						
1.	Zirconium Phosphate	Amorphous	P/Zr=0.5-2.1	$Zr(OH)(PO_4)$ $ZrO(HPO_4)$ $Zr_3(PO_4)_4$ $Zr(HPO_4)_2.H_2O$ $Zr(HPO_4)(H_2PO_4)(OH)$	-	Cs^+, Rb^+, K^+, Na^+, $Eu^{3+}, Sr^{2+}, Co^{2+}$, Ni^{2+}, Zn^{2+}	32,33,34,35, 36,37,38,39, 40,41,42,43
		Semi-crystalline	-	-	-	Li^+, K^+, H^+, Cs^+	
		Crystalline	-	$Zr(HPO_4)_2.H_2O$	-	$Sr^{2+}, UO_2^{2+}, Ce^{3+}$, Na^+, Cs^+, NH_4^+	
2.	Zirconium pyrophosphate	Amorphous	P/Zr=2.0, 2.5-2.8	-	-	$Cu^{2+}, Ni^{2+}, Ca^{2+}$ Na^+, Fe^{2+}, Mg^{2+}	44,45
3.	Zirconium hypophosphate	Amorphous	Zr/P=0.57	-	-	For multivalent metals	46,47,48
4.	Zirconium Vanadate	-	-	-	-	-	49

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
5.	Zirconium polyphosphate	Amorphous	-	-	-	For alkali metals (in NH_4^+ form) & Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+} (in H^+ form)	50,51,52
6.	Zirconium antimonate	Amorphous	-	-	-	Na^+,K^+,NH_4^+,Rb^+, Cs^+, Li^+	53,54
7.	Zirconium arsenate	Amorphous	As/Zr=1.53-1.96	-	-	Cs^+, K^+,Na^+ (at pH 2.6); Na^+,K^+,Cs^+ (at pH 4.6)	55,56
		Crystalline	-	$Zr(HASO_4)_2.H_2O$	-	-	
8.	Zirconium molybdate	Amorphous	Zr/Mo=0.5-2.0	-	2.18 for K^+ 2.43 for Cs^+	-	57
9.	Zirconium tungstate	Amorphous	Zr/W=1.0-0.44	-	-	Cs^+,Rb^+,K^+, Na^+, Li^+	48,58,59 60
10.	Zirconium tellurate	Amorphous	-	$Zr(H_2TeO_6).4H_2O$	2.80	-	61,62
11.	Zirconium oxalate	Crystalline	-	$Zr(OH)C_2O_4H$	2.50	Na^+,Cs^+,Rb^+,K^+	63

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
12.	Zirconium silicate	Amorphous	-	-	3.18	$Th^{4+}, Sm^{3+}, Ca^{2+}$	64,65
13.	Zirconium ferrocyanide	Amorphous	Fe/Zr=0.55	-	0.95	Li^{+}, Na^{+}, NH_4^{+}	66
14.	Zirconium oxide	Amorphous	-	$ZrO_2.4.7H_2O$	1.00	Ca^{2+}, Ba^{2+}	67,68
	ii) Thorium based ion-exchangers						
15.	Thorium phosphate	Crystalline	-	$Th(HPO_4)_2.3H_2O$	3.70	-	69,70
16.	Thorium oxide	Amorphous	-	$Th(OH)_n nH_2O$	2.00	$Na^{+}, Rb^{+}, Ca^{2+}, Sr^{2+}$	71,73
17.	Thorium arsenate	Crystalline	-	$Th(HAsO_4)_2.H_2O$	-	-	74
18.	Thorium molybdate	Amorphous	-	-	0.75	$Fe^{3+}, Zr^{4+}, Pb^{2+}$	75
19.	Thorium tungstate	Amorphous	Th/W=2.0	$Th(OH)_2(HWO_4)_2.nH_2O$	0.46	Cs^{+}, K^{+}, Na^{+}	76
20.	Thorium antimonate	Amorphous	Sb/Th=3.65		0.32	Cu^{2+}, Pb^{2+}	77

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
	iii) Titanium based ion-exchangers						
21.	Titanium phosphate	Amorphous	P/Ti=0.6-2.0	$(TiO)_{0.535}(H_2PO_4)_{0.369}(OH)_{1.77}1.11H_2O$	-	-	78,79,80, 81,82,83, 84,85
				$TiH_2(PO_4)_2.4H_2O$	7.5	Cs^+	
				$Ti_3(PO_4)_4$	-	-	
		Crystalline	-	$Ti(HPO_4)_2.H_2O$	7.15	-	
22.	Titanium arsenate	Amorphous	-	$Ti(HAsO_4)_2$-$2.5H_2O$	1.00	Pb^{2+},Cu^{2+},Ba^{2+}, Sr^{2+},Zn^{2+},Cd^{2+}	86,87,88, 89
		Crystalline	-	$Ti(HAsO_4)_2.H_2O$	5.80	-	
23.	Titanium antimonate	Amorphous	Sb/Ti=1.0	-	0.70	Rare earth metals	90,91
24.	Titanium molybdate	Amorphous	No/Ti=0.5-2.0	-	0.8-1.60	Pb^{2+},Ba^{2+},Tl^+,K^+	92,93
25.	Titanium tungstate	Amorphous	-	-	0.4-0.76	Cs^+,Mg^{2+},Ca^{2+}	93,94,95
26.	Titanium selenite	Amorphous	Ti/Se=1.39	-	0.78	Cd^{2+}	96
27.	Titanium vanadate	Amorphous	V/Ti=4.0	$Ti_3(V_3O_9.1.5H_2O)_4.13H_2O$	0.68	Sr^+	97
28.	Titanium tellurate	Amorphous	Te/Ti=2.06	-	-	-	98
29.	Titanium ferrocyanide	Amorphous	$Fe(CN)_6^{4-}$/Ti=2.0	-	1.40	Cs^+	99

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
30.	Titanium silicate	Amorphous	-	-	-	-	100
31.	Lead phosphate	Crystalline	-	$Pb(HPO_4)_2.H_2O$	4.79	-	101
32.	Lead tungstate	Amorphous	W/Pb=2.5	W/Pb=2.5	1.0	Cu^{2+}	102
33.	Lead ferrocyanide	Amorphous	-	Pb2[$Fe(CN)_6$]	-	Cs^+,Co^{2+}	103
	iv) Cerium (IV) based ion-exchangers						
34.	Cerium phosphate	Amorphous	P/Ce=1.03-1.95	$Ce_3(OH)_8(H_2PO_4)_4$	2.90	Cs^+.Rb^+,K^+, Na^+,Li^+	104,105, 106,107, 108,109
		Micro-crystalline	P/Ce=1.3	Ce-O-$Ce(HPO_4)_3.H_2O$	-	Cs^+,Na^+,Ag^+	
		Crystalline	-	$Ce(HPO_4)_2.H_2O$	5.20	-	
35.	Cerium phosphate sulphate	Crystalline	Ce:P:S 2:1:2	$Ce_2O(HPO_4)_{3-x}(SO_4)_x.4H_2O$ where 0 x 1	-	Na^+,Ag^+,Sr^{2+}, Cs^+,Ca^{2+}	104,110, 111
36.	Cerium arsenate	Micro-crystalline	As/Ce=2.0	$Ce(HAsO_4)_2.2H_2O$	4.25	-	112,113
37.	Cerium molybdate	Amorphous	-	-	0.96	-	114
38.	Cerium antimonate	Amorphous	Sb/Ce=0.33	-	1.23	Hg^{2+}	115

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
39.	Cerium tungstate	Amorphous	Ce^{4+}/WO^{2-}_4 =0.49	-	0.89	Hg^{2+},Tl^{+}	116
	v) Tin(IV) based ion-exchangers						
40.	Stannic phosphate	Amorphous	P/Sn=1.25-1.50	-	1.20-1.44	Cs^{+},Rb^{+},K^{+}, Na^{+},Li^{+},Cu^{2+}, Zn^{2+},Ni^{2+},Co^{2+}	117
		Crystalline	-	$Sn(HPO_4)_2.H_2O$	7.90	-	
41.	Stannic arsenate	Amorphous	Sn/As=1.8	-	0.79-0.94	Al^{3+}, Ga^{3+},In^{3+}	118,119
		Crystalline	-	$Sn(HAsO_4)_2.H_2O$	-	-	
42.	Stannic molybdate	Amorphous	Sn/Mo=1.10	-	1.00	Pb^{2+}	120
43.	Stannic tungstate	Semi-transparent	Sn/W=0.33	-	0.58	Co^{2+},Ba^{2+},Ni^{2+}, Pb^{2+},Ni^{2+},Cu^{2+}, Sr^{2+}	121
44.	Stannic antimonate	Amorphous	Sb/Sn=1.0	-	0.75	Cu^{2+},Ni^{2+},Co^{2+}	122
45.	Stannic selenite	Amorphous	Sn/Se=1.33	$(SnO_4)(OH)_2(SeO_3)_3.6H_2O$	0.75	Li^{+},Na^{+},K^{+}	123
46.	Stannic ferrocyanide	Amorphous	Sn/Fe=3.0	$(SnO)_3(OH)_3.HFe(CN)_6.3H_2O_n$	2.02	K^{+},Ba^{2+},Na^{+}	124
47.	Stannic vanadate	Amorphous	Sn/V=1.0	$[Sn(OH)_3]_3V_3O_9.4H_2O$	0.85	K^{+},Na^{+},Li^{+}	125

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
48.	Stannic silicate	Amorphous	-	-	1.98	Cu^{2+},Zn^{2+},Co^{2+}	126
49.	Stannic oxide	Amorphous	-	-	-	Fe^{3+},Ni^{2+},Mn^{2+}	127-130
50.	Nickel ferrocyanide	Amorphous	-	-	-	Cs^{+},Mn^{2+}	131,133
51.	Cobalt ferrocyanide	Amorphous	-	-	-	Ag^{+}	134,136
52.	Lanthanum oxalate	Amorphous	-	-	-	-	137
	vi) Chromium(III) based ion-exchangers						
53.	Chromium phosphate	Amorphous (Polyfunc-tional)	P/Cr=0.6-1.0	$Cr_2O_2HPO_4$ $Cr_2O(HPO_4)_2$	5.90	Na^{+},K^{+},Rb^{+},Cs^{+}, Ca^{2+},Sr^{2+},Ba^{2+}	138,139
54.	Chromium tripoly-phosphate	Glassy	Cr/P=1:2.48	$Cr_5(P_3O_{10})_3.nH_2O$	-	Cs^{+},Rb^{+},K^{+},Na^{+}, H^{+}	140
55.	Chromium arsenate	Amorphous	As/Cr=1.98	$Cr_2O_3(H_3AsO_4)_4.3H_2O$	0.63	Zr^{4+}, Hf^{4+}	141
56.	Chromium molybdate	Amorphous	Mo/Cr=1.90	$Cr_2O_3(H_2MoO_4)_4.8H_2O$	0.34	Pb^{2+},Ga^{3+}	141
57.	Chromium tungstate	Amorphous	W/Cr=1.92	$Cr_2O_3(H_2WO_4)_4.11H_2O$	0.02	Th^{4+},Hf^{4+}	141

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
58.	Chromium antimonate	Amorphous	Sb/Cr=2.95	$Cr_2O_3 \cdot 3Sb_2O_5 \cdot 22H_2O$	0.42	Pb^{2+}, Co^{2+}	141
59.	Chromium tellurate	Amorphous	Te/Cr=0.2	-	-	-	98
60.	Chromium ferrocyanide	Amorphous	Cr/Fe=0.66	-	-	-	142
	vii) Iron(III) based ion-exchangers						
61.	Ferric phosphate	Amrophous	P/Fe=2.0	$FeH(HPO_4)_2 \cdot nH_2O$	0.77	$Pb^{2+}, Eu^{3+}, Ga^{3+}$	143
62.	Ferric pyro-phosphate	-	-	$Fe_4(P_2O_7)_3$	-	In^{3+}	144
63.	Ferric arsenate	Amorphous	As/Fe=1.33	-	0.80	K^+, Na^+, Li^+	145
64.	Ferric antimonate	Amorphous	Sb/Fe=2.4	-	0.82	Cd^{2+}	146
65.	Ferric tungstate	Amorphous	Fe/W=1.0	-	0.84	Ce^{4+}	147
66.	Ferric ferrocyanide	Amorphous	-	-	3.60	Cs^+	148,149
67.	Ferro silicate	Amorphous	-	-	-	-	150

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
	viii) Aluminium(III) based ion-exchangers						
68.	Aluminium triphosphate	-	Al/P=0.5-0.66	-	2.50	-	151
69.	Aluminium vanadate	-	-	$(Al_2O_3)_n(V_2O_5)_m$ n/m = 2.0-0.5	-	-	152
70.	Aluminium antimonate	Amorphous	Al/Sb=4.2	-	1.14	Ag^+,UO_2^{2+},Ba^{2+}, Ti^{4+}	153,154
	ix) Other acidic salts						
71.	Tantalum arsenate	Amorphous	Ta/As=2.8	-	1.09	Na^+,K^+,Ba^{2+}	155
72.	Tantalum phosphate	Amorphous	-	-	-	-	156
73.	Tantalum antimonate	Amorphous	Ta/Sb=1.3	-	0.99	Na^+,K^+, NH_4^+	157
74.	Tantalum pentaoxide	Amorphous	Ta/Sb=1.30	-	0.99	NH_4^+,Na^+,K^+,Va^+	158
75.	Niobium arsenate	Amorphous	Nb/As=1.96	-	1.06	Cd^{2+},Mn^{2+},Al^{3+}	159
76.	Niobium phosphate	Amorphous	-	-	-	-	160-161
77.	Niobium antimonate	Semi-crystalline	Nb/Sb=1.40	-	1.10	Mg^{2+}	162-163
		Crystalline	-	$Nb_2.Sb_3.O_{11}.(OH)_3.2H_2O$	0.90	NH_4^+,	

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
78.	Niobium vanadate	Amorphous	-	-	-	Ce^{4+}, Eu^{3+}	164
79.	Tungston ferrocyanide	Amorphous	W/Fe=1.32	-	1.02	-	165
80.	Molybdate ferrocyanide	Semi-crystalline	Fe/Mo=2.3	$(H_4Fe(CN)_6)_4(MoO_3(H_2O)_n)_{16}$	12.0	Cs^+	166
81.	Antimonic acid	Crystalline	-	$Sb_2O_5.4H_2O$	1.28	K^+, Li^+	167
82.	Uranyl hydrogen phosphate	-	-	$UO_2HPO_4.4H_2O$	-	Cs^+, Rb^+, K^+	168
83.	Germanium(IV) phosphate	Crystalline	-	$Ge(HPO_4)_2.H_2O$	7.08	-	169
84.	Vanadium ferrocyanide	Amorphous	V/Fe=0.93	-	2.36	Cs^+, Rb^+	170
85.	Bismuth tungstate	Amorphous	Bi/W=0.5	-	0.74	Pb^{2+}	171
86.	Bismuth nitrate	Amorphous	-	-	-	-	172
87.	Bismuth tillurate	Amorphous	Te/Bi=0.70	$Bi_4(H_2TeO_8)_3.nH_2O$	3.20	-	173

Sl. No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
88.	Stannous ferrocyanide	Amorphous	Sn/Fe=1.0	$SnO.H_4Fe(CN)_6.2.5H_2O$	2.03	$Cu^{2+}, Ni^{2+}, Mn^{2+}$	174
89.	Zinc ferrocyanide	Amorphous	Zn/Fe=1.98	$Zn_2Fe(CN)_6$	6.10	Cs^+	175
90.	Zinc phosphate	Amorphous	-	-	-	-	176
91.	Zinc silicate	Amorphous	Zn:Si 1:2	-	2.30	-	177

Table - B

Properties of some three component ion exchangers

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
1.	Zirconium Phospho silicate	Amorphous	-	-	2.2	Cs^+	178-180
2.	Zirconium molybdo phosphate	-	-	-	1.6	-	181
3.	Zirconium Titanium phosphate	Crystalline	Zr/Ti = 3.25	$Zr_x Ti_{1-x} (HPO_4)_2$ $H_2O = 0.77$	6.87	-	182
4.	Zirconium Molybdo Vanadate	-	Zr : V : Mo 1.68:1.00:0.88 3.31:1.00:0.28 6.15:1.00:0.82	-	-	Li^+, Na^+	183
5.	Zirconium Phthalo Phosphate	-	-	-	-	-	184
6.	Zirconium Sulfosalicyclo-phosphate	-	-	-	-	-	185
7.	Zirconium Cerium Phosphate	-	-	-	-	-	186

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selecti vity	References
8.	Zirconium arseno phosphate	Amorphous	Zr : As : P	$Zr(HASO_4)$	5.85	Rb^+, Ag^+, Ti^+	187-188
9.	Zirconium Iodophosphate	-	-	-	1.41	-	189
10.	Zirconium arseno silicate	Crystalline	-	-	-	Hg^{2+}	190
11.	Zirconium Phosphoiodate	Amorphous	-	-	-	-	191
12.	Zirconium Silico Molybdate(IV)	Amorphous	-	-	-	-	192
13.	Zirconium(IV) seleno phosphate	Amorphous	Zr : Se : P 5.06:2.0:4.05	-	1.51	-	194-195
14.	Zirconium Iodomolybdate	Amorphous	-	-	-	-	196-197
15.	Zirconium arsenate vanadate	Amorphous	-	-	-	-	198
16.	Titanium Phospho silicate	Amorphous	TiO_2 : PO_4:SiO_4 1.76:1.97:9.54	-	2.50	Zr^{4+}, Nb^{5+}. Cs^+	199

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selecti-vity	References
17.	Titanium Molybdo phosphates	-	-	-	-	-	200
18.	Titanium Vanado phosphates	-	-	-	-	-	201
19.	Titanium tungsto arsenate	Amorphous	-	-	0.86	Rb^{+},Pb^{2+}	202,203
20.	Titanium arseno phosphate	-	-	-	-	-	204
21.	Titanium arseno molybdate	Amorphous	Ti : As : Mo 2.2:1.0 : 1.6	-	1.48	La^{+}, Ce^{3+}	205
22.	Stannic arseno phosphate	Amorphous	Sn : As : P 1.7:1.0:1.0	$[(SnO_2)(H_3AsO_4)_3 (H_3PO_4)]_nH_2O$	-	-	206
23.	Stannic vanado phosphate	Crystalline	-	-	1.98	Ba^{2+},Cu^{2+}	207
24.	Stannic vanado arsenate	Amorphous	Sn : V : As 1.94:1.14:1.10	-	1.20	Ba^{2+}	208

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selecti vity	References
25.	Stannic molybdo Arsenate	Amorphous	Sn : Mo : As 2 : 1 : 1	-	1.40	-	209
26.	Stannic tungusto Arsenate	Amorphous	Sn : W : As 12 : 5 : 2	-	1.06	Ba^{2+}, Cu^{2+}	210
27.	Stannic Iodophosphate	-	-	-	1.60	Hg^{2+}	211,212
28.	Stannic Molybdo silicate	Amorphous	-	-	0.65	Th^{4+}	213
29.	Stannic tungusto selenate	Crystalline	Sn : Se : W 7 : 1 : 18	$[(SnO_2)(HSeO_3)(HWO_4)_{18}]45H_2O$	0.88	Th^{4+},Ce^{3+}	214
30.	Stannic borato phosphate	Amorphous	-	-	1.10	-	215
31.	Stannic borato sulphate	Amorphous	-	-	0.55	-	216
32.	Stannic arsenato borate	Amorphous	-	-	0.99	-	216

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selecti vity	References
33.	Thorium phospho silicate	Amorphous	-	$(ThO_2H_3PO_4 . H_4SiO_4).6H_2O$	1.66	Hg^{2+}	217
34.	Lead Strontium phosphate	-	-	-	-	-	218
35.	Iron(III) Iodophosphate	-	-	-	1.03	-	219
36.	Pyridium 12 tungusto arsenate	-	$(C_5H_5NH)_3W_{12}AsO_4$	-	-	Ag^+, Cs^+	220
37.	Pyridium 12 Molybdo arsenate	-	-	-	-	-	221
38.	Stannic Vanadopyro phosphate	-	-	-	3.17	-	222
39.	Stannic borato tungustate	Amorphous	-	-	-	-	216
40.	Stannic borato molybdate	Amorphous	Sn : B : Mo 1 : 1 : 1	-	1.12	Zr^{4+}, Th^{4+}	216

S.No.	Material	Type of exchanger	Composition	Emperical formula	I.E.C. meq/g	Selectivity	References
41.	Stannic seleno arsenate	Amorphous	Sn : Se : As 1 : 1 : 1.02	-	1.44	Hg^{2+}	223
42.	Stannic seleno phosphate	Amorphous	-	-	-	-	224,225
43.	Stannic arseno silicate	-	-	-	-	-	226

For a complete description of a material as an ion exchanger its physical characterization should be made on the basis of the following properties.

1. Ion exchange capacity
2. Resistance towards acids and bases
3. Chemical composition, and
4. Potentiometric studies

Ion exchange capacity is one of the most fundamental properties for the characterization of an ion exchange capacity is by giving the number of ionogenic groups per specified amount of the ion exchanger in H^+ or Cl^- form. The characteristic constant thus obtained is called scientific weight capacity and is expressed in terms of the miliequivalents per gram dry H^+ or Cl^- form exchanger. This is a characteristic constant of the ion exchange material and is independent of the experimental conditions. Other definations are also used for various types of capacities, which depend on the experimental conditions. The capacities of strong cation exchangers are readily determined by direct methods. The equilibrium ion exchange capacity of a strong cation exchanger is determined by direct titration of the exchanger in H^+ form with a strong base. This method is not reliable for the determination of ion exchange capacity of weak ion exchangers. In such cases the exchanger is first converted to H^+ form, then the equilibrium ion exchange capacity is determined by pH-titrations. The maximum ion

exchange capacity equal to the number ionogenic groups per specified amount of the ion exchanger may be determined by simple column operation. In this method the electrolyte solution is passed over the ion exchanger in H^+ form at a slow rate and the liberated acid is titrated with a standard base solution. Other methods may also be used for the determination of ion exchange capacity of the solid ion exchanger. For example a gravimetric method[227], which offers for many ion exchangers the advantage of relatively high accuracy with a very simple equipment. This method is based only on the difference in weighing without any chemical determination of ions.

The ion exchange material must be studied for its resistance towards acids to check its limitations.

The ion exchange materials may behave either as monofunctional or polyfunctional. The behaviour (monofunctional or polyfunctional) of ion exchangers can be determined by potentiometric titrations. The shape of the titration curve indicates whether the exchanger is monofunctional or polyfunctional. Such curves on zirconium phosphate with alkaline earth metal hydroxides have been studied by Alberti et al.[228] in detail. They observed that the titration curves are strongly affected by hydrolysis of the exchanger and precipitation of insoluble phosphates. The degree of conversion at which phosphate precipitation begins depends on the alkaline earth metal ions and the following values were obtained : Ca^{2+} 70% exchange, Sr^{2+} 80% exchange

and Ba^{2+} 100% exchange. No exchange was found with $Mg(OH)_2$ due to its large hydrated ionic radius. Alberti et. al.[229] also studied the forward and reverse Na^+ - K^+ exchange isotherms and found that Na^+ - K^+ exchange in aqueous solution is a two step process with partial phase solubility. They also observed that zirconium phosphate prepared either bythe refluxing procedure or by direct precipitation procedure, exhibit similar X-ray powder patterns but possess different ion exchange behaviour.[230]

The unity of the ion exchange materials can be developed on the basis of the following studies.

1. Distribution of counter ions between the exchanger and solution phases.
2. Thermodynamics
3. Kinetics, and
4. Analytical applications.

The affinity of an ion exchanger for a counter ion A is given quantitatively by the distribution coefficient, Kd which is defined as -

$$Kd = \frac{\text{No. of m.eq. of A in exchanger phase } g^{-1}}{\text{No. of m.eq. of A in solution phase } ml^{-1}}$$

The distribution of an ion between the exchanger and solution phases is a direct measure of selectivity. Usually the ion exchanger takes up certain ions in preference to the other counter ions present in the solution. The selectivity is an important factor for the study of separations and it may depend mainly on -

1. Donnan potential
2. Sieve action, and
3. Complex formation

The distribution coefficient is a practical guide to the separation procedure. By determining Kd values under varying experimental conditions, it is possible to select most suitable conditions for separating small amounts of various ions. The general use of distribution coefficient is made in the elution technique used in separations. The rate at which ions move in an ion exchange column depends on their distribution coefficients to two different ions at low concentrations is called the separation factor which can be used to evaluate the ease of separating the two ions.

The ion exchange materials have found a number of important analytical applications. An introductory description on the application of natural and synthetic ion exchangers has been given by Kuroda[231]. The analytical applications of ion exchange continue to increase at exponential rate. Newer and newer areas of application are actively being sought day after day. Ion exchange has found its application in -

1. Water pollution control - Purification of water.
2. Removal of interfering ions.
3. Recovery of precious metals.
4. Preparation of deionized water
5. Water softening
6. Determination of total salt content of a solution.

7. Separation of metal ions.
8. Separation of organic and biologically important substances.
9. Concentration of trace constituents.
10. Specific spot tests.
11. Location of end point in titrations.
12. Gas chromatography, electrophoresis and solid state separations.
13. Preparation of ion selective electrodes, and
14. Preparation of ion exchanger fuel cells.

The most important applications of ion exchangers is purification of water. The water pollution is increasing day by day due to increase in industrialization and urbanization. In its natural state water always contains dissolved impurities. Organic matters and suspended solids are more hazardous than minerals. Ion exchange technology is useful for removing these ionic species, when present in ionic form. The great simplicity of the technique makes ion exchange very attractive and inexpensive tool for the purpose. Purification on large can be made by passing the sample solution through the ion exchanger bed which takes up certain materials in preference of others.

The removal of one or more interfering ions by replacement with an innocuous ion is an obvious application of ion exchange. This technique can also be utilized to recover traces of useful elements from dilute solutions. The elements present in ionic form are exchanged by an

equivalent amount of counter ion present in the exchanger and subsequently eluted fromthe exchanger by suitable electrolytic reagents. Thus, a trace amount of an ion is isolated or concentrated from a large volume of aqueous solution into a small volume of the eluent. This is a common step in the determination of trace metals in water, copper in milk[232] or the recovery of precious metals. This technique has been used for the isolation and identification of the new trans uranium elements[233-234] and for the enrichment of isotopes.[235-236]

Water softening is perhaps the most common application of ion exchange. Calcium, magnessium, iron and several other charged cations are replaced by sodium, when hard water is passed through a column of sodium from ion exchanger. The softened water then contains sodium salts which are innocuous for most of the uses. Sodium is chosen because it is harmless in water and because the ion exchanger can be easily regenerated by using a saturated solution of common salt.

Completely deionized water is prepared by passing the raw water through a cation exchanger which replaced all cations with hydrogen ion and then through on anion exchanger which replaces all anions with hydroxide ion. In effect, the salts are replaced with the ions of water. The two exchanger can be combined in a single mixed bed so that the water never becomes to acidic or basic as it might if passed through the two ion exchangers separately. The

determination of total salt content of a solution is considerably simplified by conversion of the cations to hydrogen ion or the anions to hydroxide ion, followed by simple acid base titration.

Ion exchange being a concentration and separation technique finds its use in water analysis to concentrate the trace quantities and separate[237-238] one substances from the other. Ion exchange is especially advantageous for the separation of metal ions with similar properties for which specific methods are not available. For example alkali and alkaline earth metals are always difficult to determine in a mixture, but can be readily separated in an ion exchange column. Ion exchangers have been used to solve previously unsolvable problems such as the separation of rare earths[239-240]. Taylor and Urey have performed partial separation of lithium isotopes[241]. Ion exchange columns now provide pure rare earth compounds on commercial scale.

The versatility of ion exchange methods has been proved by achieving the separation of organic and biologically important substances. The most impressive example is the separation of the complex mixtures of amino acids[242-243]. Proteins[244], nucleic acids[245], carbohydrates and their derivatives[246-247], alcohols[248-249], glycols[250], carbonyl compounds[251-252], ethers, amines, hydrocarbons and phenols have also been separated on ion exchange columns.

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CHAPTER - II

SYNTHESES AND ION EXCHANGE PROPERTIES OF STANNIC SILICO PHOSPHATE

INTRODUCTION

The present work was undertaken to synthesize an ion exchanger involving two anionic species with one basic species i.e. stannic silico phosphate. Such materials are also termed as double salts. The method of synthesis was finalized by a comparative study of different samples. Chemical composition has been determined and the material has been characterized by IR analysis. The ion exchange behaviour has also been investigated and the selectivity is examined in terms of Kd-values of certain metal ions. The possible separation are also listed.

EXPERIMENTAL

Reagents : Stannic chloride (Loba), sodium phosphate dibasic anhydrous (Sarabhi), sodium silicate (Loba).

Apparatus : An electric temperature controlled SICO shaker and Bauch and Lomb spectronic 20 (USA) were used for shaking and spectrophotometric determination respectively. Elico pH meter model Li-10 (India) was used for pH measurements.

Synthesis : Various samples of exchanger were prepared by mixing of 0.1 M stannic chloride, 0.1M sodium phosphate dibasic anhydrous and 0.1M sodium silicate under different sets of conditions as listed in Table 1. On the basis of maximum yield and high capacity 2:2:1 volume ratio was chosen for synthesis. The white precipitate so obtained was allowed to settle overnight, washed with distilled water and dried at 60°C. The dried product was immersed in distilled water when it broken down easily into small granules. It was washed several times with distilled water and then dried in an air oven at 60±1°C.

Cation Exchange Capacity : Ion exchange capacity for H^+ ion was determined by taking stannic silicophosphate in H^+ form and then eluting with 1.0M sodium nitrate solution. The H^+ ions liberated in the effluent were titrated with 0.1M NaOH solution. Metal ion capacity was determined by shaking 1.0g of the exchanger with 20 ml .1M aqueous solution of metal nitrate and titrating the metal ion left in the supernatent liquid with .01M EDTA solution.

pH Titration : Stannic silico phosphate is a cation exchanger. The pH-titration were performed in alkaline medium. To study the cation exchange behaviour, .05N solution of different alkali (NaOH, KOH, and LiOH) and .05N solution of their respective salts were shaken with .5 gm of the exchanger. The mixing ratio of two solutions were taken in such way that the total volume remained 50 ml in all cases.

Chemical Composition : A 500 mg of stannic silico phosphate was dissolved in 100 ml solution containing 5 ml sulphuric acid and 15 ml of hydrochloric acid. Tin in this sample was reduced by Pb powder and determined iodometrically[1]. For the determination of phosphate,[2] phosphate is precipitated as magnessium ammonium phosphate. The magnessium content of precipitate can then be titrated with standard EDTA solution to give indirect determination of phosphate. Silicate was determinated by spectrophotometric method.[3] Silicate give intense yellow colour with solution of molybdate in an acid medium due to the complex silicomolybdic acid. The complex is reduced to molybdenum blue. The mole ratio of Sn:Si:P is found to be 6:0.9:3.

Distribution Coefficient :

Distribution coefficients for different metal ions were determined by bach process. 1 ml of 0.1M of metal nitrate solution and 19 ml of water were added in 250 ml *erlenmayer flask. 0.5 gm of the exchanger was than added in*

these flasks. These flasks were then shaken for 4 hours in a shaker for obtaining complete equilibrium. The cations left in the supernatent liquid were determined by titration with .005m solution of EDTA. Total amount of cations were also determined without equilibration. Kd values were calculated according to the formula

$$Kd = \frac{\text{m moles of metal species/gm of the exchanger}}{\text{m moles of metal species/ml of the total volume of the resultant solution}}$$

Kd values of different metal ions were determined in aqueous solution. The results are summarized in TAble-4.

IR Studies :

Infra-red spectrum of exchanger was performed using KBr disc on IR-408, Shimadzu Corporation Kyoto, Japan.

RESULTS

Synthesis : Stannic silico phosphate was prepared under different sets of condition. These different sets of condition are given in TAble-1.

Table - 1

Condition of Preparation and Properties of Stannic Silico phosphate

Sample	Molarity of reagents			Mixing ratio	pH	Properties	
	Sodium phosphate	Stannic chloride	Sodium silicate			Nature of precipitate	Ion exchange capacity meq/g
1.	0.1	0.1	0.1	1:1:1	1.9	Mild Precipitation	0.76
2.	0.1	0.1	0.1	1:2:1	1.9	Mild Precipitation	0.6
3.	0.1	0.1	0.1	1:2:2	1.7	Mild Precipitation	0.94
4.	0.1	0.1	0.1	1:1:2	1.7	Mild Precipitation	0.8
5.	0.1	0.1	0.1	2:1:1	1.5	Mild Precipitation	0.8
6.	0.1	0.1	0.1	2:2:1	1.5	Thick white Precipitation	1.0
7.	0.1	0.1	0.1	1:2:1	1.7	Mild Precipitation	0.6

Cation Exchange Capacity : Cation exchange capacity and metal ion capacity of stannic silicophosphate are given below -

Table - 2

Cation Exchange Capacity of Stannic Silico Phosphate

Serial No.	Cation	Exchange Capacity meq/g
1.	H^+	1.0
2.	Ca^{2+}	0.8
3.	Cd^{2+}	0.3
4.	Co^{2+}	0.6
5.	Zn^{2+}	0.4
6.	Cu^{2+}	1.20
7.	Pb^{2+}	1.44
8.	Al^{3+}	1.20
9.	Mg^{2+}	0.28

pH Titration : Stannic silico phosphate is a cation exchanger. pH-Titration were performed in alkaline medium. Figure-1 shows pH-titration curve in alkaline medium with their respective salts. Table-3 shows the pH-Titration in alkaline medium.

Table - 3

Potentiometric Titration for Stannic Silico Phosphate

S.No.	Volume of .05 NaOH (Total volume of .05 NaOH + .05N NaCl) = 50 ml	pH
1.	0	2.8
2.	1	2.9
3.	2	3.05
4.	3	3.3
5.	4	3.5
6.	5	3.7
7.	6	3.95
8.	8	4.45
9.	10	4.90
10.	15	6.45
11.	20	7.1
12.	25	7.50
13.	30	8.40
14.	35	8.90
15.	40	8.90
16.	45	9.30
17.	50	10.25

Kd-Values : Distribution coefficient for different metal ions are given in TAble-4. These Kd values for different metal ions are determined in aqueous solution.

Table - 4

Kd values for some ions on Stannic Silico Phosphate

S.No.	Metal ion	Kd values ml g^{-1}
1.	Cu^{2+}	240.0
2.	Ni^{2+}	44.0
3.	Co^{2+}	56.0
4.	Al^{3+}	200.0
5.	Cd^{2+}	26.40
6.	Ca^{2+}	72.0
7.	Mg^{2+}	29.2
8.	Zn^{2+}	52.0
9.	Pb^{2+}	493.2
10.	Mn^{2+}	44.0

Possible Separation : Table-5 shows the possible separation on the basis of the difference in Kd values. The Kd values are given in parenthesis.

Table - 5

Possible Separation on the basis of Kd-values

S.No.	Separation of		Separation from	
1.	Cu^{2+}	(240)	Mg^{2+}	(29.2)
2.	Al^{3+}	(200)	Cd^{2+}	(26.4)
3.	Pb^{2+}	(493.2)	Mg^{2+}	(29.2)

Chemical Composition : The mole ratio of stannic silico phosphate is found to be (Sn:Si:P) 6:0.9:3.

IR Studies : Figure-2 shows the spectrum of stannic silico phosphate on KBr disc.

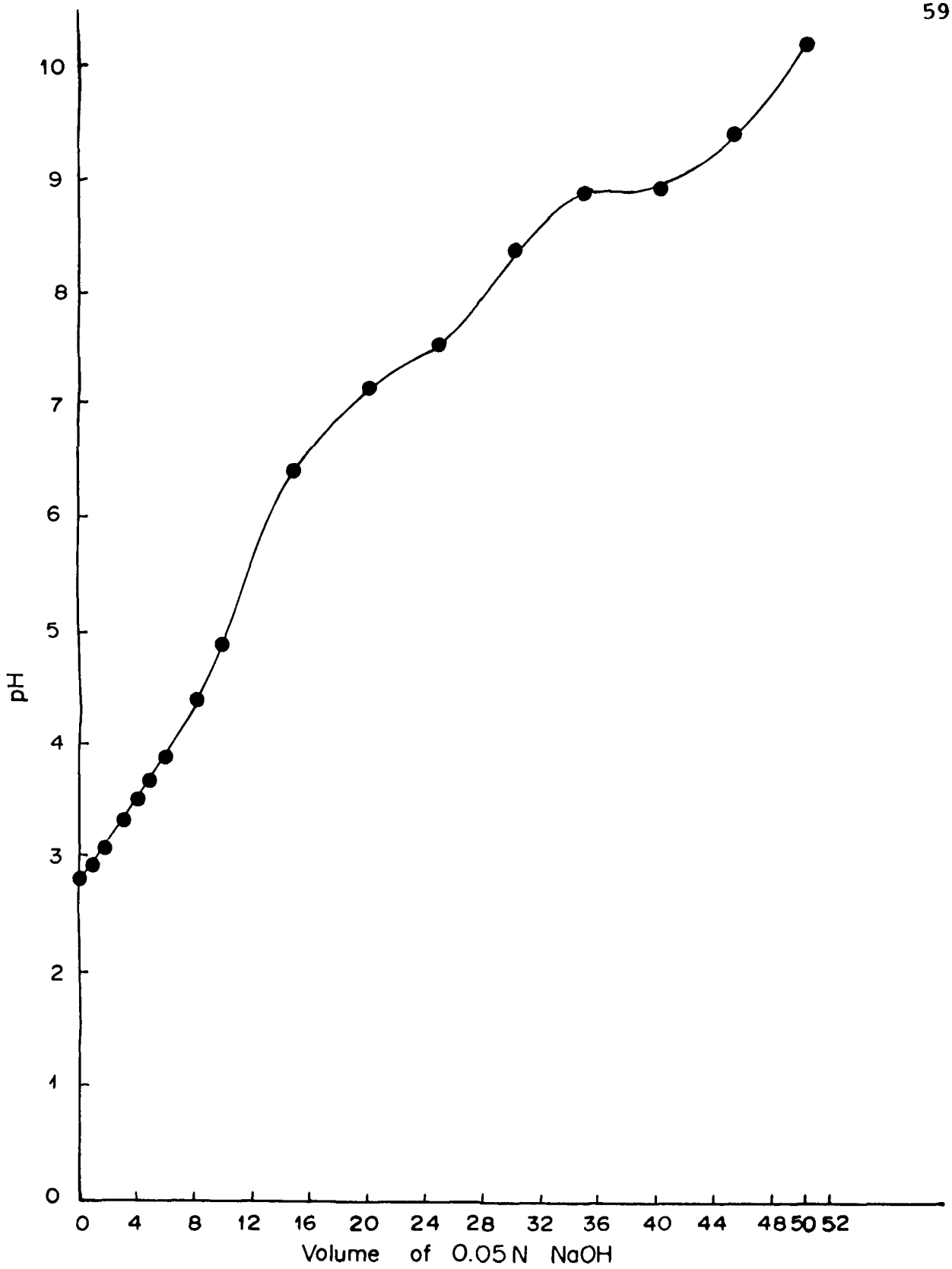

Fig. 1 : pH - Titration curve for Stannic Silico Phosphate .

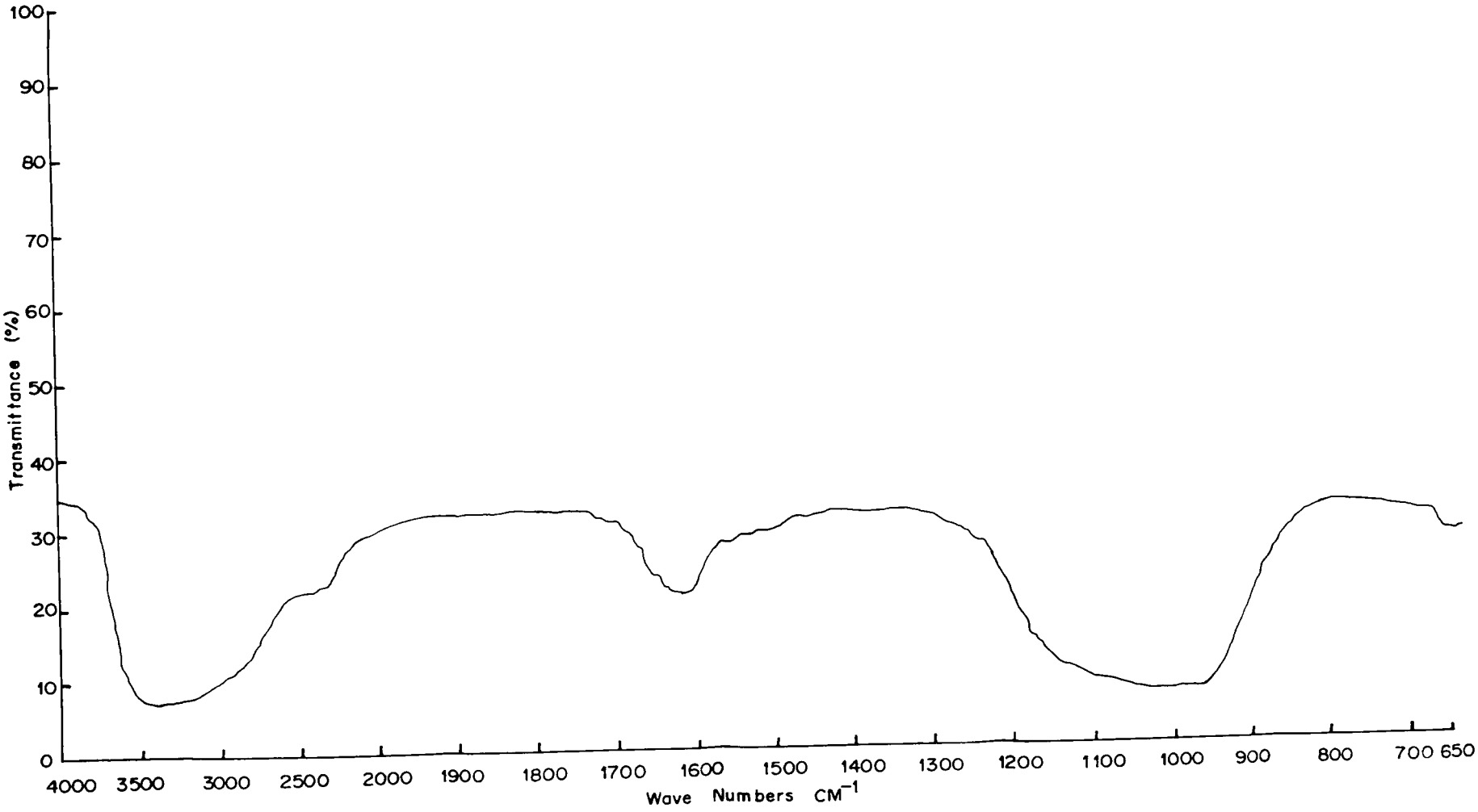

Fig. 2 : I R Spectrum of Stannic Silico Phosphate .

DISCUSSION

The results of Table-1 indicates that stannic silico phosphate prepared under different conditions. These samples are obtained in different yield and possess different ion exchange capacity. The sample No. 6 possess maximum yield and shows the highest capacity. Hence this sample was chosen for the detailed studies.

The material stannic silico phosphate behaves as a weak cation exchanger. The ion exchange capacity varies with the nature of the metal ion (Table-2). The maximum capacity was obtained for Pb^{2+}.

The results of pH-titration presented in Table-3 and plotted in Figure-1. The results of pH titration indicate that the stannic silico phosphate is a bifunctional weak inorganic cation exchanger. The two steps are responsible for ionizing hydrogen ions from two different acidic groups.

The results of chemical composition reveal that the mole ratio of Sn:Si:P is 6:0.9:3 which is apparently equal to 6:1:3 for sample No. 6.

The results of Table-4 for the determination of distribution coefficient for certain metal ions. The results reveal that the ion exchanger shows the different selectivity. The highest Kd-values obtained for Pb^{2+}. This is in accordance with the high value of ion exchange capacity for this metal ion.

On the basis of the difference in Kd-values the separations can be achieved for certain pairs of metal ions. The results presented in Table-5 indicates such possibilities.

It is quite evident from the IR spectrum plotted in Figure-2 that the material contains water molecules and metal oxygen bands as is fully discussed below. The structure of stannic silico phosphate is a complicated one like some silicates with other metal ions. An indication of possible structure may be discussed in the light of IR spectrum of the compound. The IR spectrum of the material shows -

The band around 3500 cm^{-1} is very strong bond which can be attributed to OH-stretching frequency.

A medium band around 1640 cm^{-1} can be attributed to H-O-H bending.

The band around 950-1200 is a mixed pleatue where the peaks due to silicate and phosphate are merged together.

A trend of absorption after 700 may be due to Sn-O stretching.

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